

Oxidation of diselenide bond with sodiumtetrachloroaurate (III): Significance in chemotherapy

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Abstract

Gold(III) reacts with selenocystamine (diselenide) and immediately breaks the diselenide-bond as observed by ^{13}C NMR spectroscopy. It is also observed that diselenide is more reactive to gold(III) compare to its analogous disulfide (cystamine) molecule. The results are compared with similar diselenide and disulfide molecule with other gold(I) drugs.

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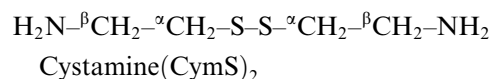
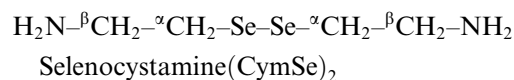
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Although the use of gold-based drugs, chrysotherapy, has been an important form of treatment for rheumatoid arthritis for over half a century, our knowledge of the reactions of gold(I) and gold(III) with biologically important ligands is very limited [1]. Gold(I) compounds are used for the treatment because gold(III) complexes are considered too toxic for medicinal uses [1]. However, a number of gold(III) compounds have been prepared and evaluated as potential anticancer agents [2]. The oxidation of cystine and other disulfides by gold(III) is already being reported by Shaw III et al. [3]. It was observed that cystine itself was capable of reducing gold(III) to metallic gold. While the mechanism of the medicinal activity of gold drugs remains elusive, there is evidence to suggest that redox pathways could be involved.

The oxidative pathologies that have been noted for rheumatoid arthritis and the ease by which gold(I) thiolates undergo oxidation suggest several possible redox roles in the anti-inflammatory response and/or in deleterious secondary reactions [4].

This range of potential biological activity points to the need of better understanding the reactivity of gold sulfur and selenium complexes in order to establish the possible mechanistic pathways, as well as to suggest pathways that are likely [2–4].

In order to understand the reactivity of disulfides and diselenides we undertook the reactions of diselenide with gold(III). We have already established earlier that diselenide is at least 100 times more reactive with $(\text{Et}_3\text{P})_2\text{Au}^+$ than disulfide [5]. Therefore, it would be of interest to study the reactivity of gold(III) with disulfide and diselenide molecules.



Selenocystamine dihydrochloride (CymSe)₂ and its analogous disulfide cystamine (CymS)₂ were obtained from the Sigma Chemical Co. $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ and D_2O were purchased from the Fluka Chemical Co. ^{13}C NMR spectra were recorded on a Jeol JNM-LA 500 NMR spectrometer operating at 125.65 MHz with ^1H

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